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VAPOR-PHASE INFRARED ABSORPTIVITY COEFFICIENT OF ISOPROPYL METHYLPHOSPHONOFLUORIDATE

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We measured the vapor-phase absorptivity coefficient of isopropyl methylphosphonofluoridate in the mid-infrared (4000-550 cm^{-1}) at a spectral resolution of 0.125 cm^{-1}. The chemical used in the feedstock was subjected to a rigorous analysis by gas chromatography-mass spectrometry and nuclear magnetic resonance to verify its purity. We describe the experimental method used to acquire the individual spectra that were used to produce the composite spectrum, summarize the statistical uncertainties in the data, and provide a comparison to similar data from another laboratory.

15. SUBJECT TERMS

Infrared	FTIR	Absorptivity coefficient	Quantitative
GB	Sarin	Saturator cell	Vapor-phase
Isopropyl methylphosphonofluoridate			

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EXECUTIVE SUMMARY

We measured the vapor-phase absorptivity coefficient of isopropyl methylphosphonofluoridate (GB) at a spectral resolution of 0.125 cm^{-1}. We used saturator cells suspended in a temperature controlled liquid bath to generate continuous streams of GB diluted in nitrogen, which werc sent to a variable path White cell and measured using a high resolution research grade Fourier transform infrared spectrometer. The purity of the feedstock was verified by gas chromatography/mass spectrometry and nuclear magnetic resonance. The concentration of GB in the vapor was determined with a gravimetric method. Eleven spectra at different concentration-pathlength products were processed line by line through least squares analysis using MatLab® to produce the absorptivity coefficient of the compound and the statistical uncertainty in the data. Uncertainties in the data, expanded to a confidence interval of 2σ ($P = 0.95$), are Type-A: 1.3% and Type-B: 2.6% of the absorptivity coefficient. An inter-laboratory comparison of the data is presented.

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PREFACE

The work described in this report was performed under the direction of the Detection Capability Officer, Defense Threat Reduction Agency Joint Science and Technology Office. This work was started and completed in August 2005.

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VAPOR-PHASE INFRARED ABSORPTIVITY COEFFICIENT OF ISOPROPYL METHYLPHOSPHONOFLUORIDATE

1.   INTRODUCTION

We report the high resolution vapor-phase absorptivity coefficients of isopropyl methylphosphonofluoridate (GB) in the spectral range of 4000-550 cm^{-1} in units of (μmol/mol)$^{-1}$m^{-1}, as well as the uncertainties in the data.

Synonyms for this compound include 1-methylethyl methylphosphonofluoridate, GB, and Sarin. It has the CAS Registry Number 104-44-8 and is indexed under the name: phosphonofluoridic acid, methyl-, 1-methylethyl ester. The molecular formula is $C_4H_{10}FO_2P$ and it has a molecular weight of 140.09. The structure is shown in Figure 1.
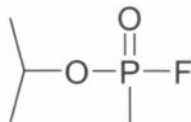

Figure 1. Molecular Structure of GB

Sarin is listed by the Organization for Prohibition of Chemical Weapons (OPCW) as a Schedule 1 organophosphonate nerve agent. It is a liquid at room temperature, with a vapor pressure of 2.46 Torr at 25 °C and a boiling point of 150.2 °C.[1] Sarin was first synthesized in Germany in 1938.

2.   EXPERIMENTAL PROCEDURES

2.1   Instrumental Details.

The system used to generate the continuous vapor stream was an adaptation of the saturator cell (Glassblowers Inc., Turnersville, NJ) method developed at the U.S. Army Edgewood Chemical Biological Center for measuring the volatility of chemical warfare (CW) agent related compounds.[2]

The method, modified to generate continuous streams of chemical compounds for obtaining quantitative vapor-phase infrared (IR) spectra, has been used to measure the absorptivity coefficients of benzene,[3] as well as a variety of CW agent related compounds. [4,5,6] The saturator passes a stream of nitrogen carrier gas, obtained from the boiloff of a bulk liquid nitrogen tank, across a conical alumina wicking mechanism in a glass holder filled with the analyte. A saturated vapor-liquid equilibrium of the analyte on the downstream side of the saturator cell results with the concentration of the analyte determined by the temperature of the liquid phase. By suspending the saturator cell in a constant temperature bath, the concentration of the analyte can be predicted by its vapor pressure at the temperature of the bath. The apparatus used in the Quantitative Fourier Transform Infrared (FTIR) Laboratory uses a Brooks

Model 5850S (Brooks Instrument Co., Hatfield, PA) mass flow controllers to maintain a constant flow to the saturator cell, along with a second mass flow controller to add diluent to the stream, providing an additional means of adjusting the concentration of the compound delivered to the White cell of the FTIR. Linearity of the S series mass flow controllers is adjusted using a second order polynomial, resulting in accuracies of approximately 1% or better of rate at flows ≥25% of full scale.

Spectra were obtained with a Bruker Model IFS/66V (Bruker Optics, Billerica, MA) FTIR. The instrument is equipped with both deuterated triglycine sulfide and mercury-cadmium-telluride (HgCdTe) detectors and is capable of obtaining spectra with a maximum spectral resolution of 0.1125 cm^{-1} (unapodized). The spectra in this report were acquired with the HgCdTe detector. The interferograms were recorded from 15798-0 cm^{-1} with a resolution of 0.125 cm^{-1}. Absorbance (log base-10) spectra were processed with boxcar apodization and 2X zero filled to obtain a data spacing of 0.0625 cm^{-1}. The instrument is equipped with a variable path White cell. The experimental data used pathlengths ranging from 2.727 to 10.66 m. Data were acquired at a speed of 60 KHz using the HgCdTe detector. Single beam spectra of the CW agent were ratioed against spectra of clean, dry nitrogen. To minimize the effects of nonlinearity in the detector, the interferograms were processed using the proprietary Opus® nonlinearity correction function. All interferograms have been archived enabling further post-processing of data.

Temperature and pressure data were recorded using National Institutes of Standards and Technology (NIST) traceable digital manometers and thermometers, and all data have been archived. Concentration-pathlength products (CL) were computed in units of μmol/mol(m) (ppm-m). A differential pressure manometer had previously been used to measure the dynamic pressure in the White cell with gas flowing into the cell. The ambient pressure was plotted versus the differential pressure. The resulting equation was used to correct the readings from the ambient pressure manometer to the pressure in the White cell. The concentration-pathlength data were corrected to 296 K and 1.0132×10^5 Pa (760 Torr) using the ideal gas law.

2.2   Feedstock.

The feedstock used in the experiments was obtained through the CASARM program under lot number G-U-6184-CTF-N at a purity stated in the certificate of analysis of 98.7 ± 1.9 wt% by titration. Analysis by of the neat material diluted in solvent by gas chromatography-mass spectrometry (GC-MS) indicated 0.5% diisopropyl methylphosponate, 0.08% methylphosphonic difluoride, 0.04 diisopropyl phosphorofluoridate, and two other phosphorous impurities at 0.02%. Nuclear magnetic resonance (NMR) analysis (^{31}P) showed a purity of 99.1 wt%. Of the reported impurities, several were either significantly more volatile than the GB, thus eluting early in the operation of the saturator cell, or less volatile, being retained in the saturator cell and not contributing significantly to the vapor stream. Samples of the vapor output collected with sorbent tubes for analysis by gas chromatography (GC) using a GC with a flame ionization detector (GC-FID) coupled directly to the effluent of the White cell indicated a purity of 99.8%. This was consistent with an independent analysis (^{31}P) by our NMR laboratory using an internal standard that returned a purity of 99.6 ± 1.2 wt%.

3.   RESULTS AND DISCUSSION

        Five trials were run to obtain spectra at eleven concentration-pathlength products. A trial is defined as filling and weighing the saturator cell, suspending it in the bath, applying a stream of nitrogen for a measured time, acquiring several spectra, stopping the nitrogen and removing it from the bath, and reweighing the saturator cell after drying the exterior surfaces and re-equilibrating to room temperature. The trials were conducted at a bath temperature of 20 °C, with the exception of the fourth trial, for which the bath was set to a temperature of 19 °C.

        The composite spectrum (absorptivity coefficient) was computed using spectra with concentration-pathlength products ranging from 24 to 633 μmol/mol(m) (corrected to 296 K and 101325 Pa). As an initial check of the quality of the data, Beer's Law plots of two spectral lines, 1326 and 1021 cm^{-1}, were calculated using MatLab. At least for these two spectral lines, the data appeared to be well fitted, with no points lying outside of the 95% confidence limits for either a repeated set or a repeated single x or the 95% confidence limits for a Grubbs Test for Outliers (Figures 2 and 3).
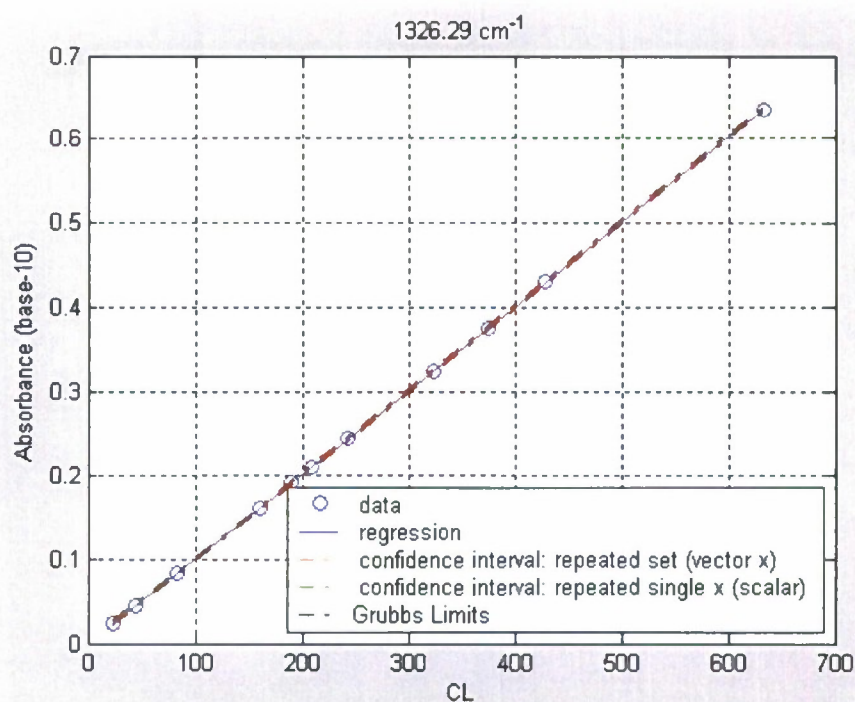

Figure 2. Beer's Law Plot of 1326 cm-1 Line in the Vapor-phase Spectrum of Isopropyl
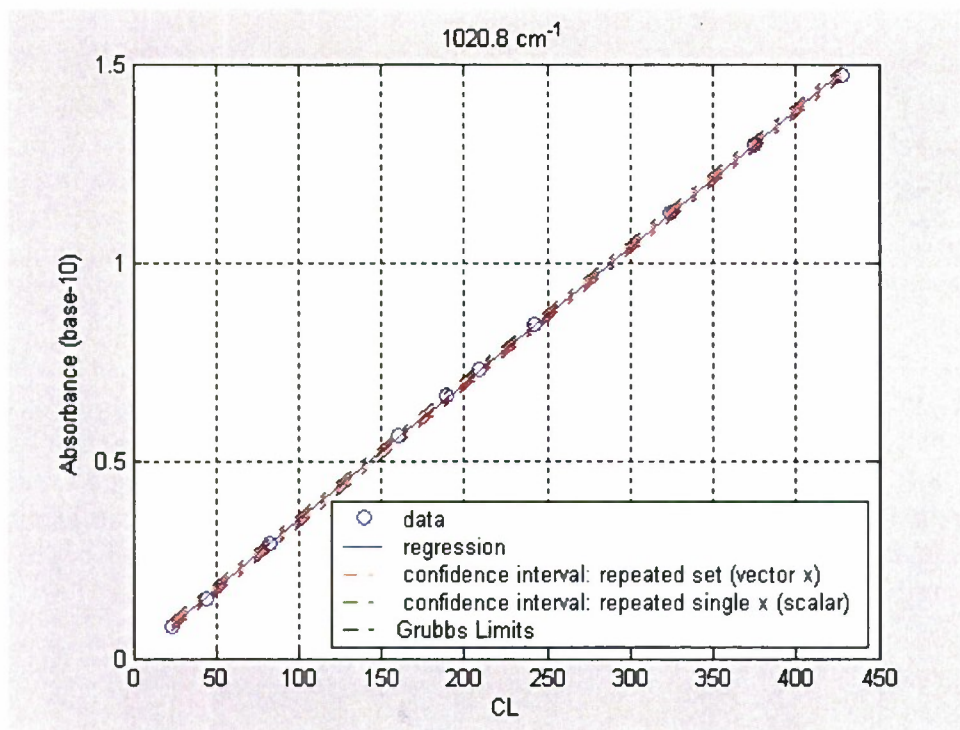   Methylphosphonofluoridate, with the Abscissa in Units of μmol/mol(m)

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Figure 3. Beer's Law Plot of 1021 cm-1 Line in the Vapor-phase Spectrum of Isopropyl Methylphosphonofluoridate, with the Abscissa in Units of μmol/mol(m)

The absorptivity coefficient (α) and uncertainty (Type-A, 2σ) were computed line by line within the spectral range of 4000-550 cm^{-1} using a MatLab program written in-house. Values of (A = -log$T$) >1.5 are normally assigned a weight of zero. Because A in all cases was <1.48, all values of A were weighted at 1. Figure 4 is the plotted absorptivity coefficient (α) and uncertainty (U_a). The figure is plotted with α in (μmol/mol)$^{-1}$m^{-1}. To obtain α in (mg/m²)$^{-1}$, multiply the values in the ordinate of Figure 3 by 0.1724. This factor is derived from eq 1 using the molecular weight of GB (140.09).

$$\frac{m^2}{mg}\left(\frac{24.15}{mw}\right)=\frac{mol}{\mu mol(m)}\tag{1}$$

Figure 5 is a plot of absorptivity coefficients (abscissa) and fractional (Type A, U_A, 2σ) uncertainties (mantissa). Figure 6 is a plot of absorptivity coefficients (abscissa) and statistical (Type A, U_A, 2σ) uncertainties (ordinate). Figure 6 also includes a best fit of the data points obtained by least squares, which is an approximation of U_A. $\approx$ ax + b. For the fitted line in Figure 6, the coefficients are: a = 6.77 X 10^{-3} and b = 1.16 X 10^{-6}. The coefficients can also be seen in Table 1. A listing of absorptivity coefficients for selected bands may be seen in Table 2.
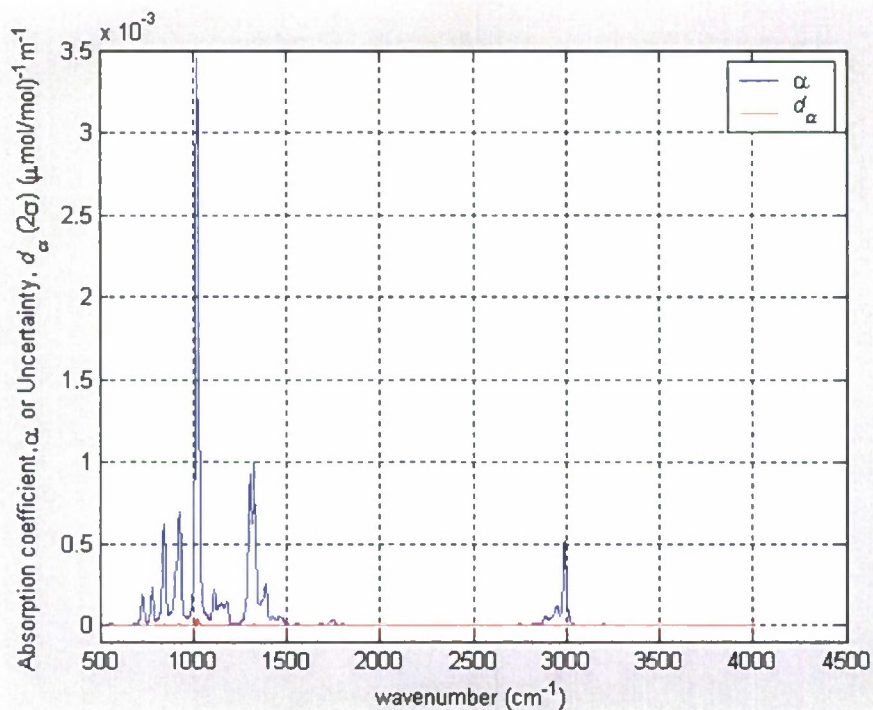
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Figure 4. Absorptivity Coefficient and Type-A Uncertainty (2σ) of Isopropyl
Methylphosphonofluoridate

Table 1 provides the absorptivity coefficients in $(\mu mol/mol)^{-1}m^{-1}$ and $(mg/m^2)^{-1}$ for selected bands in units of wavenumber and micrometers (μm).

Table 1. Absorptivity Coefficient of Sarin for Selected Bands

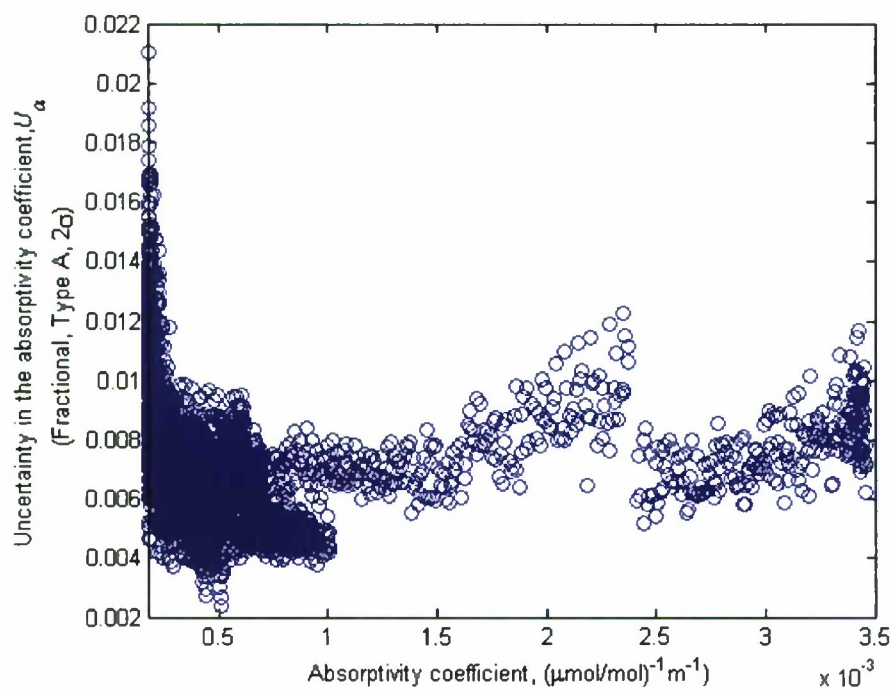| Wavenumber, cm^{-1} (Wavelength, μm)	Absorptivity coefficient, $(\mu mol/mol)^{-1}m^{-1}$ $[(mg/m^2)^{-1}]$
927.1 (10.8)	6.905×10^{-4} $[1.19 \times 10^{-4}]$
1020.9 (9.80)	3.456×10^{-3} $[5.96 \times 10^{-4}]$
1326.4 (7.54)	1.004×10^{-3} $[1.73 \times 10^{-4}]$

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Figure 5. Absorption Coefficient (Abscissa) and Type-A Fractional Uncertainty (2σ) for Isopropyl Methylphosphonofluoridate
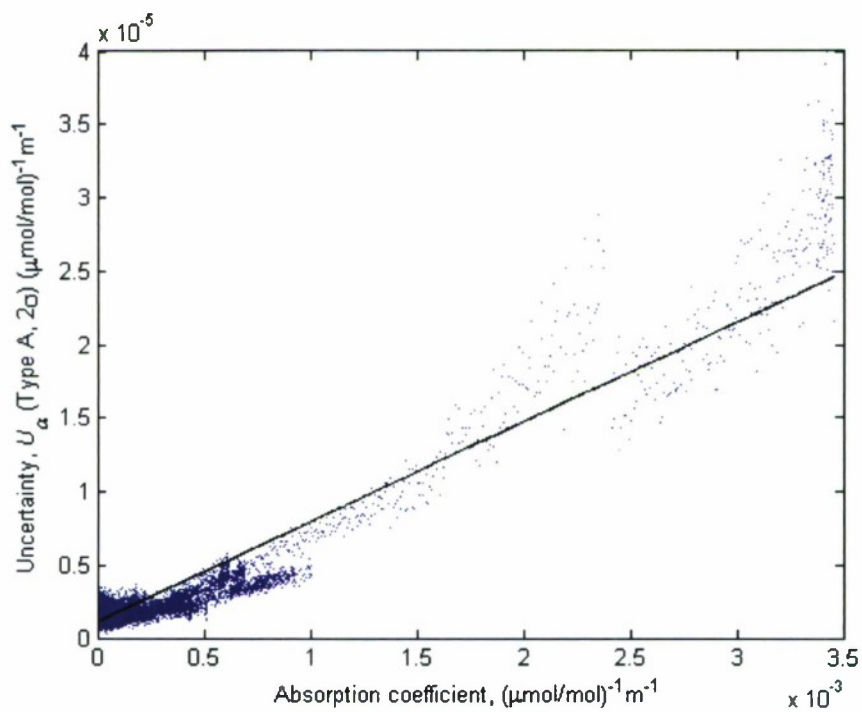

Figure 6. Absorption Coefficient (Abscissa) and Type-A Uncertainty (2σ) for Isopropyl Methylphosphonofluoridate

Table 2. Type-A Statistical Uncertainty for Isopropyl Methylphosphonofluoridate Vapor-phase Absorptivity Coefficient

Type A $2\sigma \approx ma + b$	
Slope m	Intercept b
6.77×10^{-3}	1.16×10^{-6}

Type-B estimated standard errors, along with their sources, as well as the combined Type-A and B uncertainties are provided in Table 3. The expanded combined Type-B uncertainty was computed using eq 2:

$$\Delta_B = (\Delta L^2 + \Delta T^2 + \Delta P^2 + \Delta FTIR^2 + \Delta NL^2 + \Delta MR^2)^{1/2} \times 2 \qquad (2)$$

The sources of uncertainty and their fractional values, as well as an explanation of the symbols in eq 1, are given in Table 3. Among the Type B uncertainties, the detector nonlinearity dominates at 1% (1σ).

Table 3. Uncertainties in Absorptivity Coefficient of Isopropyl Methylphosphonofluoridate from ECBC Data Where $\alpha \geq 0.000175$ $(\mu mol/mol)^{-1}m^{-1}$

Symbol	Fractional deviation	Source
ΔL	0.005	Pathlength
ΔT	0.0006	Temperature of White cell
ΔP	0.0003	Pressure
$\Delta FTIR$	0.0005	Drift in spectrometer
ΔNL	0.01	Nonlinearity in detector
ΔMR	0.0014	Mass rate
ΔD	0.005	Dilution rate
Δpurity	0.005	Purity of vapor
Δ_B	0.020	Combined type B (2σ)
Δ_A	0.013	Type A deviation (2σ)

We compared the integrated absorptivity coefficient obtained in our laboratory to data from two other sources: PNNL/Dugway[7] and Barrett and Dismukes.[8] Data are shown in Table 4. Reference 4 did not cite a reference temperature and pressure, and the data was available in electronic form only in the fingerprint region.

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Table 4. Comparison of Integrated Absorption Coefficients of GB in Spectra from ECBC and PNNL/Dugway

Range	PNNL	ECBC	B-D	(ECBC-PNNL)/ECBC	(ECBC-BD)/ECBC
		No Baseline Correction			
3085-2792	0.01973	0.01749	N/A	-0.128	
1525-600	0.18710	0.19398	0.2115	0.035	-0.090
		Baseline corrected			
3085-2792	0.01935	0.01719	N/A	-0.126	
1525-600	0.18710	0.1927	0.04172	0.029	-0.020

We noted differences in the baseline regions in the PNNL spectrum as compared to the other two laboratories, which can be seen in Figure 7. Aligning the baseline of the PNNL spectrum to more closely approximate that of the other two laboratories was only partially successful. The documentation with the data file indicated that a baseline correction had been performed on the spectrum using a seventh-order polynomial, and the factors for the polynomial were not available to us. Additionally, the PNNL spectrum appeared to have several spectral features that would be consistent with the presence of diisopropyl methylphosphonate (DIMP) in the vapor stream. A high quality reference spectrum of this compound was available from the PNNL database. Subtracting a scaled spectrum of the DIMP from the GB spectrum indicated that the compound may have contributed ~8% of the total area of the spectrum of the GB in the C-H stretch region and ~11% in the fingerprint region, where the spectral features of the DIMP are most intense relative to those of the GB. Type-A and Type-B uncertainty for the PNNL spectrum are stated at 2.4% and <10% respectively.
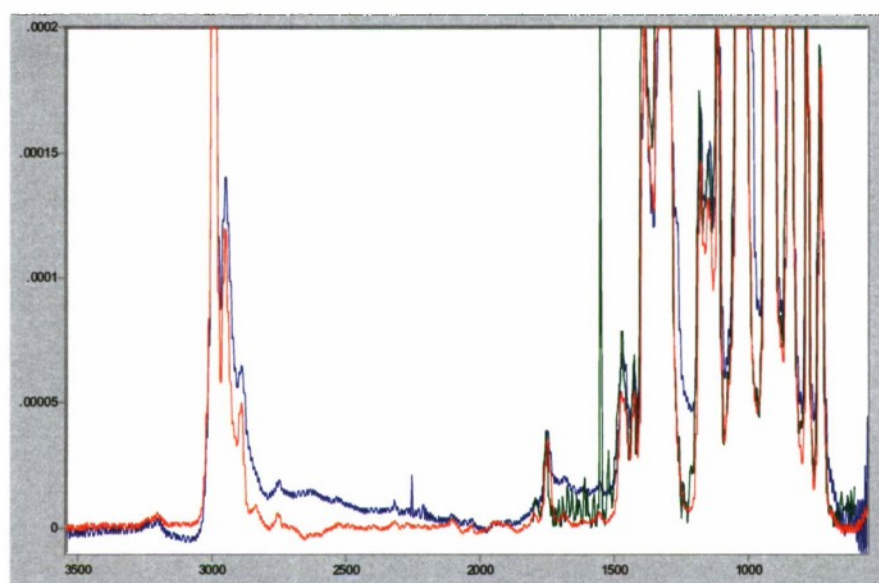

Figure 7. Absorptivity Coefficient of GB from ECBC (red), PNNL/Dugway (blue), and Barrett and Dismukes (olive), Showing Baseline Differences

4.   CONCLUSIONS

The absorption coefficient of the nerve agent Sarin, was obtained within the region of 4000-550 cm^{-1} at a resolution of 0.125 cm^{-1}. Uncertainties, expanded to 2σ, are 1.3% (Type-A) and of the absorption coefficient for bands with intensities >5% of the most intense absorption feature. An inter-laboratory comparison of the data obtained at PNNL indicated that the differences in the spectra may be explained by the presence of an impurity in the material used by PNNL to generate the spectra.

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